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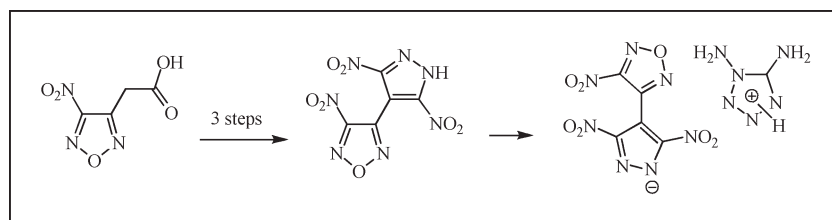
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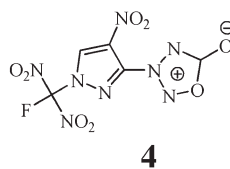
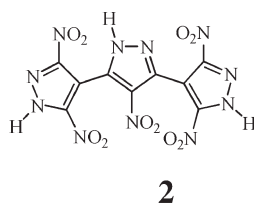
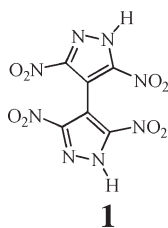


The annulation reaction of vinamidinium salt containing nitrofurazanyl moiety at the β -position gives access to the corresponding pyrazole. At nitration, two nitro groups were installed to the pyrazole ring. The synthesized 3-(3,5-dinitropyrazol-4-yl)-4-nitrofurazan **13** is strong NH acid and a new family energetic salts was prepared by direct neutralization with high nitrogen bases. Compound **13** crystallizes in the monoclinic space group $P2_1/c$, and characterized by high density of 1.979 g/cm³ (at 100 K).

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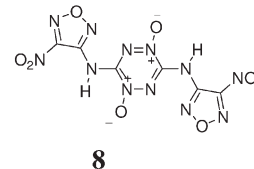
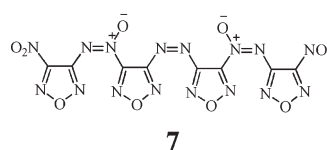
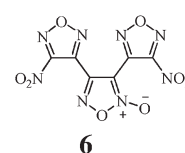
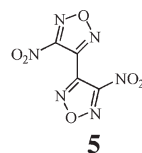
INTRODUCTION

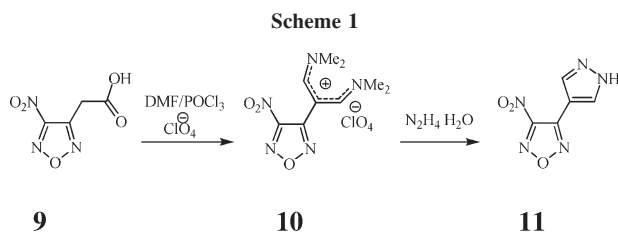
There is a need for novel high energy and density compounds for applications in industry, the military, and the space programs. More than half a century, the construction of high energy compounds based on azoles modified by explosore groups has attracted considerable interest [1]. In the last years, the investigations were directed to the search for new more effective combinations of structural fragments in such molecules. Thus, a set of nitropyrazoles, such as bipyrazoles **1** and tripyrazoles **2** [2], aza-syndones **3** and **4** [3], are of particular interest.



The high thermal and chemical stability of 1-H-3,5-dinitropyrazole compounds have made dinitropyrazole attractive building block to be utilized at construction energetic materials, which possess significant insensitivity to heat, friction, and impact. These properties are the result of hydrogen bonding between nitro group and N—H fragment of the ring. Progress in the synthesis and chemistry of nitropyrazoles has been the subject of several reviews [4].

Furazan derivatives have played a remarkably diverse role as energetic ingredients in formulation of high explosives, solid propellants, and pyrotechnic gas generators [5]. The nitrofurazans are critical class of the derivatives that have been thoroughly investigated and recently reviewed [6]. While there are a set of examples of nitrofurazans with additional furazan ring(s), for example, di- (**5**) [7], tri- (**6**) [5h,8], and tetrafurazans **7** [9], only a few examples incorporating other heterocycles (for example,





compound **8** [10i]) have been reported [5f,5j,10]. The nitrofuran moiety is excellent building block for construction of new energetic compounds.

The aim of this research was to prepare a high energy compound [11], wherein nitrofuran and 1-H-3,5-dinitropyrazole moieties are bound together by simple C—C bond. Herein synthetic approach for the preparation of the compound from nitrofuran-precursor is described.

RESULTS AND DISCUSSION

The β -substituted vinamidinium (1,5-diazapentadienium) salts are very useful synthons in organic synthesis and have been widely utilized in the construction of the pyrazole ring [12]. We anticipated that reaction of a furazan-modified vinamidinium salt with hydrazine would efficiently provide the desired pyrazolyl-furazan skeleton.

In the synthesis of the perchlorate salt **10** (Scheme 1), 3-nitrofuranan-2-carboxylic acid **9** [13] was added to phosphorus oxychloride and DMF, and the mixture was heated at 95–100°C over a period of 2 h. At the end of reaction, mixture was diluted with EtOH followed by quenching in a solution of aqueous sodium perchlorate. The crude perchlorate **10** was isolated in 67% yield, and a 51% overall yield was realized following recrystallization.

The salt **10** undergoes condensation with hydrazine in the presence of sodium acetate and acetic acid in ethanol upon heating at reflux. The desired pyrazole **11** was isolated in 78% yield following chromatography. This ring closure reaction is suitable for large-scale use and yields the pyrazole **11** in greater than 80% yield.

With the pyrazole **11** in hand, the next step was to install two nitro groups to the ring. Nitrofurananyl moiety as substituent is more powerful acceptor than trinitrophenyl group [14]. Electron-withdrawing substituents at pyrazole retarded nitration of the ring. Although several methods for nitration of pyrazoles are available [4], we desired a reasonable procedure that would be effective for a pyrazole bearing a high electron-withdrawing substituent at 4 position.

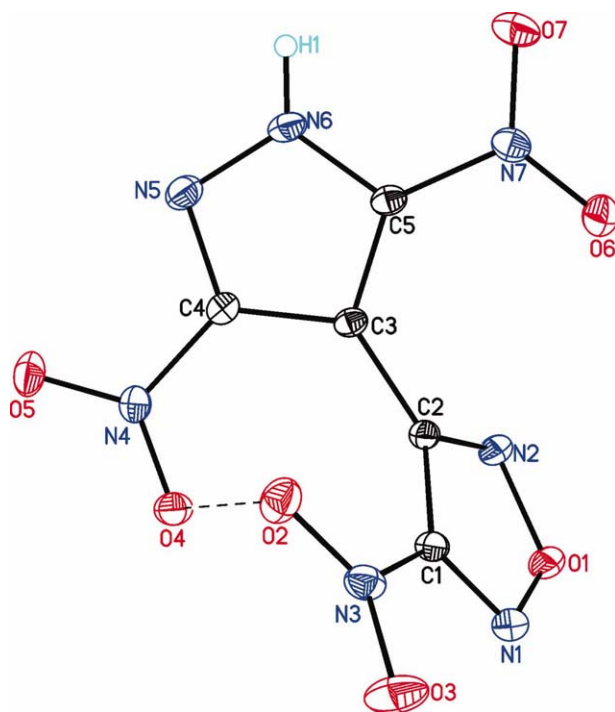
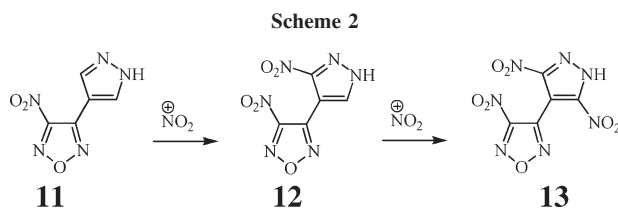


Figure 1. ORTEP view (drawn at 50% probability of thermal displacement ellipsoids) of compound **13**. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

An attempt to nitrate the pyrazole **11**, using fuming nitric acid in either acetic or trifluoroacetic acid at 75–95°C failed to yield any of the expected nitro product. However, heating at 100°C with a mixture of nitric acid and oleum, resulted in clean conversion to mononitropyrazole **12** as determined by NMR and TLC analysis. On prolonged refluxing with fuming nitric acid and oleum (20% SO_3) pyrazole **11** affords a mixture of the mononitro derivatives **12** and 3,5-dinitro derivatives **13** (Scheme 2). After 12 h, the major products obtained correspond to compound **13** (33%) as well as mononitropyrazole **12** (16%) that could be readily separated by fractional crystallization or silica gel chromatography.

Products **12** and **13** were thoroughly characterized by MS, IR, and ^1H -, ^{13}C - and ^{14}N -NMR spectra which are consistent with previously published data for related compounds [4c]. The structure of the trinitrated product **13** was firmly established by a single crystal X-ray diffraction study using a sample crystallized from HNO_3 . General view of **13** is presented in Figure 1. An asymmetric unit cell contains one molecule. Due to a sterical repulsion between nitro groups and five-membered cycles, the molecule cannot adopt planar structure, therefore pyrazole ring is rotated relative to furazan ring about C2—C3 bond (see Table 1). Such an orientation allows nitro groups to be nearly coplanar with rings to which they are bound to gain stabilization by a π -

Table 1Selected geometrical characteristics that define molecular conformation of compound **13**.

Torsional angle (°) or distance (Å)	X-ray	Theory
C1—C2—C3—C4	−64.8 (2)	−62.2
C2—C1—N3—O2	5.3 (2)	−9.7
C3—C4—N4—O4	2.2 (2)	−0.1
C3—C5—N7—O6	2.5 (2)	−3.6
O2...O4	2.9657 (13)	3.066

Comparison of experimental and theoretical (M052X/aug-cc-pvdz) data.

conjugation. An additional stabilization of the observed conformation of molecule **13** is probably provided by nonbonded contact between O2 and O4 oxygen atoms separated by a distance [2.9657(13) Å] shorter than sum of nonbonded radii (1.56 Å [15]). To obtain more information on this contact, we have carried out quantum chemical calculation of isolated molecule followed by topological analysis of electron density distribution in terms of “Atoms in molecules” (AIM) theory [16] using the AIMAll program [17]. Geometry optimization was carried out at M052X/aug-cc-pvdz level of approximation by the GAUSSIAN03 program [18]. This level of approximation was successfully utilized in our recent study on structural peculiarities of nitraminofurazans [19]. As initial geometry, we used X-ray one as well as a geometry in which two 5-membered rings are coplanar while nitro groups are oriented perpendicular. Both ways of the optimization have resulted in the same structure, which conformation is nearly identical to that observed experimentally (Table 1). Calculated O2...O4 separation is also less than sum of oxygen nonbonded radii and (3,−1) critical point (CP) which, in terms of AIM theory, corresponds to an attractive interatomic interaction was localized. Energy of O2...O4 contact estimated by the correlation between energy and potential energy density in CP [20] is equal to −2.1 kcal/mol.

As it is usually observed for high nitrogen derivatives of furazan [5e,5h,21] or pyrazole with only few (or without) hydrogen atoms [2a,22], crystal structure of trinitro compound **13** is characterized by high density (1.979 g/cm³) due to numerous close O...O, N...O, and N...N contacts

and H-bonding. The hydrogen (H1) in compound **13** forms bifurcated H-bonds to N1 and O3 atoms. These interactions are relatively weak (N6-H1...N1: N—H 0.87(2) Å, N...N 3.1221(14), H...N 2.46(2), =NHN 133(2)°; N6—H1...O3: N...O 3.1265(14), H...N 2.56(2), =NHO 124(2)°) that is normally observed for hydrogens participating in two H-bonds simultaneously. In addition to H-bonding, molecules are connected to each other by relatively strong O...O and N...O interactions. We restricted choice of nonbonded contacts (see Table 2) by those which interatomic separations are certainly less than sum of nonbonded radii (1.61 Å for N and 1.56 Å for O) [15]. By means of H-bonding and close contacts listed in left side of Table 2, molecules form layers parallel to *ac* crystallographic plane while the other shortened interactions (right side) connect layers to 3-dimensional network (see Supporting Information). The crystal structure is also stabilized by numerous slightly shortened O...O, O...N, and N...N contacts with distances at the boundary between normal and shortened ones.

Combination of the electron-withdrawing furazan ring with moieties containing acidic proton increases its acidity. Recently, a number of furazan-based acids was synthesized and utilized as anions for a preparation of energetic salts [19,23].

It should be remarked that few examples of energetic salts incorporating a nitropyrazolate anion, namely 3,5-dinitro-pyrazolate anion, has been described [24]. The pyrazole **13** synthesized in this study has three electron-withdrawing substituents on the ring and therefore appears to be a high NH acid (*pKa* = 0.65) and can be reacted with bases to form corresponding salts.

To find simple correlation of structural and electronic molecular properties with the value of *pKa* in 3,5-dinitropyrazoles we have carried out calculation of several differently substituted isolated molecules and their hydrates. Molecules considered are depicted in the form of their hydrates in Figure 2.

Upon an increase of proton acidity (decrease of *pKa*), in isolated molecules we expect the N—H bond to become more polar which should result in its elongation and an increase of the positive proton charge while in hydrates a decrease of *pKa* should lead to a strengthen

Table 2Close contacts in the crystal structure of compound **13**.

Contact	Distance (Å)	Symmetry code	Contact	Distance (Å)	Symmetry code
O1...O4	2.9707 (12)		O2...O5	2.9768 (13)	−x, 1−y, −z
O1...N2	2.9214 (14)	x, 1.5−y, 0.5+z	O5...N5	3.0122 (14)	
N2...O4	3.0353 (13)				
O1...O7	2.8317 (12)	1+x, 1.5−y, 0.5+z	O3...O3	2.959 (2)	1−x, 1−y, 2−z
O5...N3	2.8686 (14)	x, y, z−1			

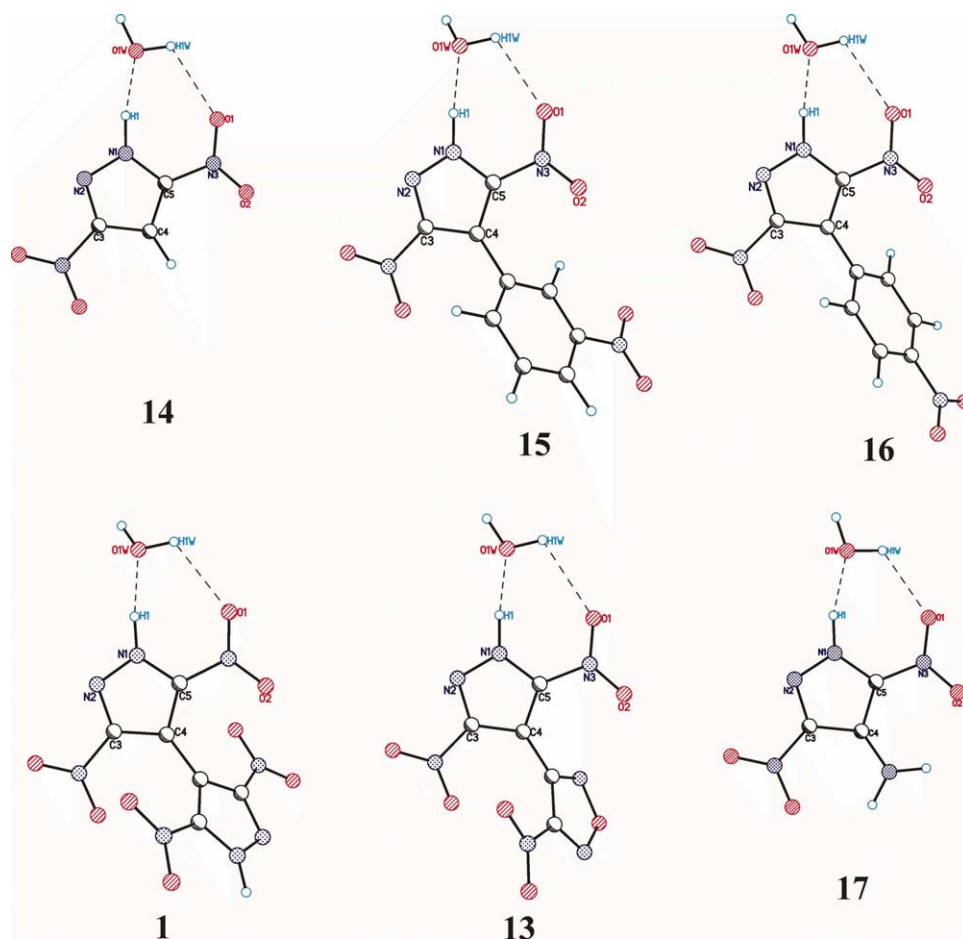


Figure 2. Model hydrates of 3,5-dinitrofurazoles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of N—H...O hydrogen bond, which is reflected in changes of its geometry (in particular in the shortening of H...O separation) and energy (E_{NHO}). The results of calculations are given in Table 3.

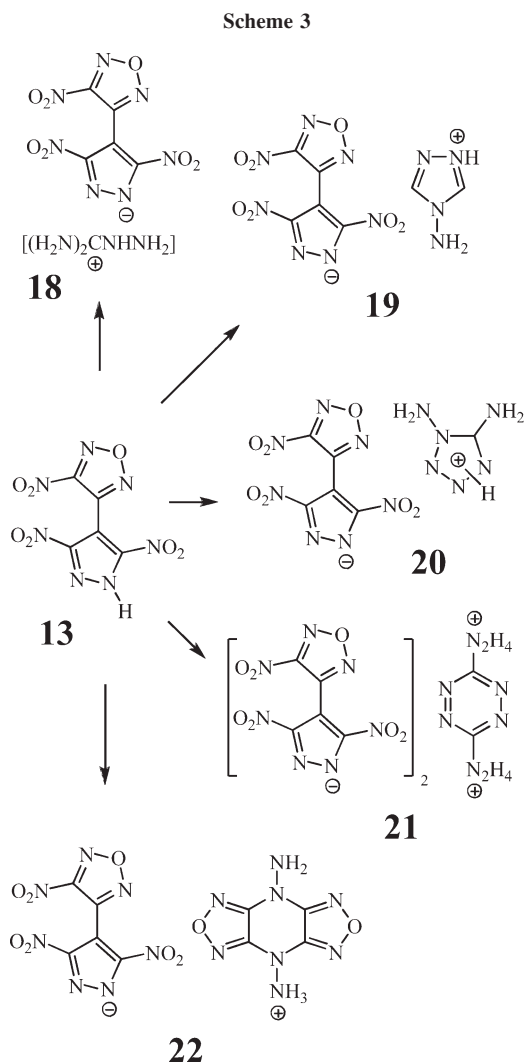
It is immediately seen that properties of isolated molecules are weakly sensitive to the acidity of hydrogen atom. Significant changes of pK_a values, for instance, between **17** and **13** are reflected in only minor changes of the proton charge (by $0.009e$ obtained by both NPA

and topological analysis of calculated electron density) and nearly constant value of N—H bond length. In the case of hydrates, in addition to expected N—H...O hydrogen bond, the water molecule also interacts with nitro-group. However this interaction is rather weak and can be considered as enforced interaction due to favorable position of the corresponding nitro-group. At the same time N—H...O bond is more sensitive to an influence of substitution in 4-position. Both the energy and

Table 3

Topological (AIM) and structural characteristics of N—H and N—H...O bonds in compounds **1**, **13–17** and their hydrates calculated by M052X/aug-cc-pvdz method.

Compound	pK_a	Isolated molecule			Hydrates	
		NPA charge of H, e	AIM charge of H, e	N1—H1 bond length, Å	H1...O1W distance, Å	E_{NHO} , kcal/mol
14	3.14 [25]	0.470	0.532	1.011	1.786	−8.17
15	—	0.473	0.534	1.011	1.773	−8.64
16	—	0.473	0.534	1.011	1.773	−8.61
1	1.79 [26]	0.474	0.535	1.011	1.762	−9.08
13	0.65	0.476	0.538	1.011	1.752	−9.24
17	3.42 [26]	0.467	0.529	1.010	1.797	−7.92



H...O distance demonstrate qualitative correlation with the pK_a value, which in turn correlates well with acceptor ability of the substituent in 4-position. It can be seen that in spite of an absence of coplanarity between pyrazole and furazan rings, 3,5-dinitropyrazole **13** forms the strongest H-bond and show high acidic properties, which allows easy formation of stable salts.

The preparation of energetic salts **18–22** (Scheme 3) were accomplished in aqueous and/or alcohol solution by reacting compound **13** with stoichiometric amounts of guanidine carbonate, aminoguanidine bicarbonate, or nitrogen-rich bases followed by fractional crystallization. Yields of purified salts between 80% and 86% were obtained. DSC and TGA studies show a family of very stable salts that decompose well above their relatively high melting points.

In conclusion, we have successfully synthesized the first reported high energy compound, wherein nitrofurazan and 1-H-3,5-dinitropyrazole moieties are bound together by simple C—C bond and have demonstrated its

use in the preparation of energetic salts with high nitrogen bases. Further application of this novel material is currently underway.

EXPERIMENTAL

Caution! Nitrofurazans are highly explosive and may be sensitive to shock or heating and must be handled with appropriate precautions.

Melting points were determined on Gallenkamp melting point apparatus and they are not corrected. Infrared spectra were determined in KBr pellets on a Perkin-Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311A instrument. $^1\text{H-NMR}$, $^{13}\text{C-}$ and $^{14}\text{N-}$ spectra were recorded on a Bruker DRXV-500 spectrometer at 300.13, 75.47, and 21.68 MHz respectively. Chemical shifts for both $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ are referred to chemical shifts for solvent (for DMSO- d_6 it is 2.50 ppm and 39.51 ppm for proton and carbon NMR, respectively) and ^{14}N NMR is referred to external standard without correction nitromethane. Analytical thin layer chromatography (TLC) was conducted on precoated silica gel plates (Silufol F₂₅₄).

All the reagents were analytical reagents purchased from commercial sources and used as received. 3-Nitrofurazanacetic acid **9** [13], 1,5-diamino-1*H*-tetrazole [27], 3,6-dihydrazino-1,2,4,5-tetrazine [28] and 4,8-diamino-4*H*,8*H*-bisfurazano[3,4-*b*:3',4'-*e*]pyrazine [29] were prepared according to literature procedures.

X-ray study of compound 13. At 100 K, single crystals of **13** ($\text{C}_5\text{H}_7\text{N}_7\text{O}_7$) are monoclinic, space group $P2_1/c$: $a = 8.4109(5)\text{\AA}$, $b = 17.9445(11)\text{\AA}$, $c = 6.3832(4)\text{\AA}$, $\beta = 109.1890(10)^\circ$, $V = 909.88(10)\text{\AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.979\text{ g cm}^{-3}$, $\mu = 0.186\text{ mm}^{-1}$. At 100 K, 9650 reflections were collected at SMART APEX2 CCD diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.71073\text{ \AA}$, graphite monochromator, ω -scans, $2\theta < 60^\circ$]. An analysis of measured intensities was carried out with the SAINT and SADABS programs incorporated in the APEX2 program package [30]. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. Only hydrogen atom was located in the difference Fourier maps and refined in isotropic approximation. 2615 independent reflections [$R(\text{int}) = 0.0273$] were used in the refinement procedure (for 176 parameters) that was converged to $wR_2 = 0.0844$ calculated on F_{hkl}^2 [GOF = 1.032, $R_1 = 0.0336$ calculated on F_{hkl} using 2187 reflections with $I > 2\sigma(I)$]. The refinement was carried out with the SHELXTL program [31]. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Any request to the CCDC should quote the full literature citation and the reference number 794,384.

2-(3-Nitrofurazan-4-yl)-1,3-bis(dimethylamino)trimethinium perchlorate 10. To a mixture of DMF (4 mL) and phosphorus oxychloride (2.2 mL) was added 3-nitrofurazanacetic acid **9** (3.46 g, 0.02 mol) at 50°C. The resulting solution was heated at 95–100°C for 2 h. The mixture was cooled to 5–10°C and diluted with ethanol (4 mL) and a solution of sodium perchlorate (2.45 g, 0.02 mol) in water (7 mL). The slurry was aged for 12 h at 0–5°C and then filtered, washing the crude solids with *i*PrOH. The crude solid was recrystallized from acetic

acid to give perchlorate **10** as a light yellow crystals (3.5 g, 51%); mp 158–159°C; ^1H NMR (DMSO- d_6) δ 2.38 (s, 6H, CH_3), 3.39 (s, 6H, CH_3), 8.13 (s, 2H, CH); ^{13}C NMR (DMSO- d_6) δ 41.0 (Me), 48.9 (Me), 80.9 (C), 145.7 (C— CNO_2), 160.4 (C— NO_2), 163.1 (CH); ^{14}N NMR (DMSO- d_6) δ -34.2 (NO_2). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{Cl}_1\text{N}_5\text{O}_7$ (339.69): C, 31.82; H, 4.15; N, 20.62. Found: C, 31.90; H, 4.18; N, 20.58.

3-Nitro-4-(pyrazol-4-yl)furazan 11. To a suspension of compound **10** (1.7 g, 0.005 mol) in 90% EtOH (11 mL) at room temperature was added NaOAc \times 3H $_2$ O (0.45 g, 0.0033 mol) and heated up to dissolving. To resulting solution a mixture of hydrazine hydrate (0.5 g, 0.01 mol), acetic acid (0.5 mL), and EtOH (3 mL) was added dropwise. The reaction was heated at reflux for 2 h and cooled to ambient. The solvent was removed in vacuo. Column chromatography of the residue on silica gel eluting with chloroform/ether (5:1) gave the pyrazole **11** as a light cream solid (0.71 g) in 78% yield; mp 38–42°C; R_f 0.35 CCl_4/MeCN (3:1). IR (KBr) ν 3156, 2964, 2840, 1612, 1568, 1516, 1384, 1364, 1320, 1288, 1220, 1160, 1104, 1044, 1028, 952, 872, 824 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 8.3 (brs, 2H, CH), 13.5 (brs, 1H, NH); ^{13}C NMR (DMSO- d_6) δ 102.7 (C), 132.0 (C—H), 138.9 (C—H), 144.5 (C— CNO_2), 159.4 (C— NO_2); ^{14}N NMR (DMSO- d_6) δ -32.7 (NO_2). Anal. Calcd for $\text{C}_5\text{H}_5\text{N}_5\text{O}_3$ (181.11): C, 33.16; H, 1.67; N, 38.67. Found: C, 33.12; H, 1.68; N, 38.65.

3-(3,5-Dinitropyrazol-4-yl)-4-nitrofurazan 13. Pyrazole **11** (1.0 g, 5.5 mmol) was added to a mixture of fuming HNO_3 (1.5 mL, 32.55 mmol) and 20% oleum (6 g) and the mixture was heated at 100°C for 12 h. After cooling, the precipitated product was filtered, recrystallized from 70% trifluoroacetic acid and dried at 130–140°C to give a colorless crystals (0.5 g) in 33.3% yield; mp 222–223°C. IR (KBr) ν 3332, 1576, 1564, 1556, 1536, 1480, 1452, 1428, 1404, 1356, 1336, 1268, 1220, 1184, 1056, 1000, 916, 880, 844, 832, 816 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 9.57 (NH); ^{13}C NMR (DMSO- d_6) δ 93.7, 142.7, 153.2, 160.0. MS m/z : 271 [M^+], 225 [$\text{M}^+ - \text{NO}_2$], 195 [$\text{M}^+ - \text{NO}_2 - \text{NO}$], 167, 150, 135, 103, 77, 54, 46; Anal. Calcd for $\text{C}_5\text{H}_1\text{N}_7\text{O}_7$ (271.11): C, 22.15; H, 0.37; N, 36.17. Found: C, 22.13; H, 0.39; N, 36.18.

3-(3-Nitropyrazol-4-yl)-4-nitrofurazan 12. At similar nitration of pyrazole **11** the compound **12** was prepared in 35% yield at reduction of reaction time to 5 h; mp 171–172°C (from CHCl_3). IR (KBr) ν 3176, 3136, 2968, 2888, 1636, 1588, 1572, 1528, 1424, 1396, 1356, 1340, 1272, 1212, 1168, 1092, 1048, 1000, 948, 836, 820 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 8.66 (s, 1H, CH), 14.8 (brs, 1H, NH); ^{13}C NMR (DMSO- d_6) δ 98.6, 135.7 (CH), 143.2 (C— CNO_2), 153.6 (NN—C— NO_2), 160.0 (ON=C— NO_2); Anal. Calcd for $\text{C}_5\text{H}_2\text{N}_6\text{O}_5$ (226.11): C, 26.56; H, 0.89; N, 37.17. Found: C, 26.62; H, 0.95; N, 37.09.

4-(3-Nitrofurazan-4-yl)-3,5-dinitropyrazolate salts 18–22 (general method). To a hot solution (~50–60°C) of compound **13** (0.1 mol) in water (10 mL) was added a equimolar amount of a hot concentrated solution of the aminoguanidinium carbonate, aminoazole, or aminoazine, respectively, in water or alcohol. The reaction mixture was heated at 50°C for 12 h, after which the solvent was removed in vacuo. All products, which were purified by recrystallization from a minimum amount of aqueous isopropanol and dried under high vacuum for 48 h at 50°C, were obtained with high yields.

Aminoguanidinium 4-(3-nitrofurazan-4-yl)-3,5-dinitropyrazolate 18. Yield: 92%; mp 231°C [dec, Tonset]; IR (KBr) ν

3410, 3340, 3285, 3060, 2795, 1665, 1655, 1640, 1580, 1525, 1495, 1380, 1355, 1335, 1325, 1200, 1165, 1110, 1055, 1015, 990, 870 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 4.81 (1H, NH), 7.4–7.5 (6H, NH_2); ^{13}C NMR (d_6 -DMSO) δ 92.8, 142.9, 156.4, 159.2, 160.1. Anal. Calcd for $\text{C}_6\text{H}_7\text{N}_{11}\text{O}_7$ (345.19): C, 20.88; H, 2.04; N, 44.63. Found: C, 20.95; H, 2.11; N, 44.60.

1-Amino-1,2,4-triazolium 4-(3-nitrofurazan-4-yl)-3,5-dinitropyrazolate 19. Yield: 95%, mp 184–186°C; IR (KBr) 3398, 3225, 3180, 2810, 1620, 1605, 1550, 1545, 1470, 1365, 1350, 1335, 1180, 1100, 1070, 1022, 990 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 4.89 (2H, NH_2), 8.77 (2H, CH); ^{13}C NMR (DMSO- d_6) δ 93.1, 142.9, 144.1, 154.3, 160.1. Anal. Calcd for $\text{C}_7\text{H}_5\text{N}_{11}\text{O}_7$ (355.18): C, 23.67; H, 1.42; N, 43.38. Found: C, 23.75; H, 1.48; N, 43.23.

1,5-Diaminotetrazolium 4-(3-nitrofurazan-4-yl)-3,5-dinitropyrazolate 20. Yield: 91% mp 196°C (dec, Tonset); IR (KBr) 3411, 3345, 3155, 2960, 2840, 1645, 1618, 1595, 1562, 1543, 1496, 1470, 1383, 1365, 1348, 1335, 1105, 1070, 1035, 1022, 977 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 5.6 (brs, NH_2); ^{13}C NMR (DMSO- d_6) δ 93.0, 143.0, 152.6, 154.3, 160.0. Anal. Calcd for $\text{C}_6\text{H}_5\text{N}_{13}\text{O}_7$ (371.19): C, 19.41; H, 1.36; N, 49.06. Found: C, 19.48; H, 1.43; N, 49.02.

3,6-Dihydrazino-s-tetrazine bis[4-(3-nitrofurazan-4-yl)-3,5-dinitropyrazolate] 21. Yield: 94%, mp 182°C (dec, Tonset); IR (KBr) 3347, 3295, 3260, 3145, 2960, 1615, 1554, 1545, 1478, 1380, 1360, 1305, 1205, 1105, 1082, 1030, 980 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 4.2 (brs), 10.7; ^{13}C NMR (DMSO- d_6) δ 92.6, 143.4, 154.5, 159.6, 161.2; ^{14}N NMR (DMSO- d_6) δ -19.3 (NO_2 -pyrazole), -34.2 (NO_2 -furazan). Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_{22}\text{O}_{14}$ (684.33): C, 21.06; H, 1.18; N, 45.03. Found: C, 21.13; H, 1.21; N, 45.00.

4,8-Diamino-4H,8H-bisfurazano[3,4-b:3',4'-e]pyrazinium 4-(3-nitrofurazan-4-yl)-3,5-dinitropyrazolate 22. Yield: 96%, mp 246–249°C; IR (KBr) 3423, 3354, 3160, 1638, 1609, 1593, 1558, 1540, 1494, 1468, 1370, 1361, 1335, 1104, 1083, 1070, 1032, 1010, 968 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 4.8 (brs, NH_2); ^{13}C NMR (DMSO- d_6) δ 92.7, 143.2, 147.7, 154.3, 160.0. Anal. Calcd for $\text{C}_9\text{H}_5\text{N}_{15}\text{O}_9$ (467.23): C, 23.14; H, 1.08; N, 44.97. Found: C, 23.20; H, 1.07; N, 44.93.

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